



**A flexible method for production of stable atomic clusters  
with variable size for chemical and catalytic activity studies**

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# Final Report

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## Summary of Progress

The goal of the present project was to set up a flexible source for production of atomic clusters with large a production rate and to measure their superconducting transition temperature. We have set up a generator based on spark discharge electrode ablation and size selected the produced clusters by mobility classification (DMA technique). The size distributions were measured on the examples of gallium (Ga) and platinum (Pt) atomic clusters. The effect of two process parameters on the distribution was determined. The total spark energy was found to have some effect on the particle size distribution, and the inlet gas temperature has a large effect. The size distributions clearly exhibit the non-scalability expected for small clusters, showing distinct peaks in the case of Pt, which we attribute to “magic numbers”, i.e. sizes of high stability. Taking the limited resolution of the present system into account, we conclude that the magic number sizes are *much* more abundant than the less stable sizes in between. This may be due to etching by oxygen impurities. For gallium, only a single peak was visible under the conditions chosen, and for platinum, conditions for uniformly sized cluster production were also found, while several peaks were present in most cases. Due to the crudeness of our model relating cluster size to mobility, we are presently unable to assign the magic numbers to the peaks observed. Ongoing studies carried out with metals of different valences will hopefully remove this ambiguity. In spite of this crudeness, we can certainly say that the chosen size range contains the size targeted for the superconductivity measurements based on the theoretical paper by Kresin, et al. [1].

We designed and set up an experiment using aerosol photoemission under variable temperature to observe the superconducting transition temperature. Unfortunately we were unable to observe the expected discontinuity due to the superconductivity transition for any chosen size due to the limitations of our experimental setup, namely the signal-to-noise ratio. Another problem may have been the a lack if clusters of the targeted size, for which the highest transition temperature is predicted, as it does not correspond to a magic number and the less stable sizes were likely etched away by oxidizing impurities. Both problems appear solvable for future research. Thus up to date, we were neither able to prove nor to disprove the predictions of Kresin et al.

Summarizing, we can say that a large step has been taken with respect to the quantities small ( $n < 100$ ) atomic clusters can be produced in. For the larger peaks, we produced about 1 mg/day. This rate could further be increased by at least 2 orders of magnitude, by increasing the spark production frequency and further from there by scaling up the spark production system. Efficient charging by photoemission could be applied for efficient size separation of virtually any material and any size of atomic clusters in the future. The mass production rate of 1 g/day is within reach with the spark generation technique in combination with a DMA. This is of great interest for applications such as catalysis and superconductivity.

## Detailed Description of Progress

The impetus of this project originates from i) the desire of producing atomic clusters in gram quantities in order to exploit their predicted properties, e.g. in catalysis and superconductivity, and ii) a paper by Kresin, et al. [1-2] predicting high superconducting transition temperatures for atomic clusters of specific numbers of atoms of a number of metallic elements. The paper predicts the highest transition temperatures for clusters of zinc and gallium atoms, with a value of ca. 170 K (ca. -103 °C) for a cluster of 56 Ga atoms ( $\text{Ga}_{56}$ ). This particular cluster was targeted in our research primarily because of this very high predicted superconducting transition temperature. Additionally, gallium presents an interesting challenge to aerosol methods for atomic cluster production.

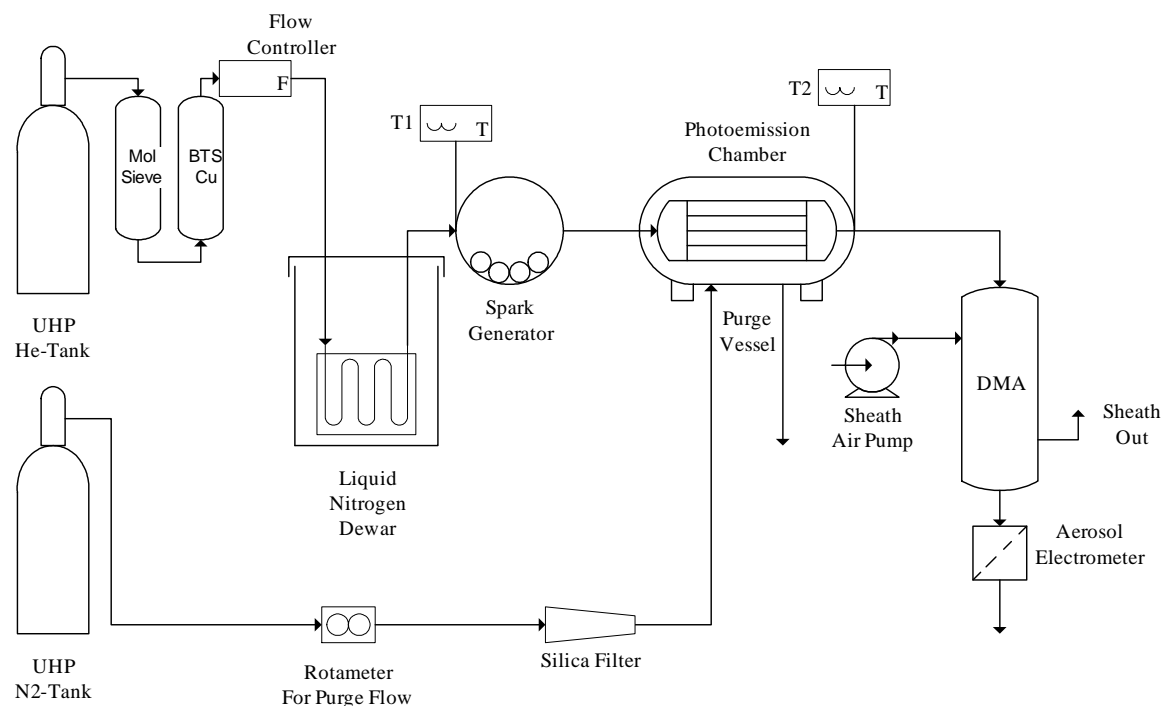
As mentioned in our interim report, we have produced and measured atomic clusters of silver using a glowing wire generator. While this type of reactor is inexpensive to build and operate, it is limited in terms of the types of materials which can be used to produce atomic clusters or nanoparticles. Because of their low vapor pressures at their respective melting points—and hence low evaporation rates - materials such as gold, sodium, and aluminum will not form a sufficiently concentrated vapor cloud from a current-carrying wire to form aerosol particles. Gallium is, in fact, at the bottom of the list of metallic elements, with a vapor pressure of  $5.72 \times 10^{-36}$  Pa at its melting point and an evaporation rate of  $1.72 \times 10^{-37}$  mol/m<sup>2</sup>/s (compared to 0.361 Pa and  $4.33 \times 10^{-3}$  mol/m<sup>2</sup>/s, respectively, for silver) [3]. Thus we chose to demonstrate and develop the capabilities of the spark discharge system to overcome this limitation of the glowing wire generator and to come up with a scalable method, promising much higher production rates. For Ga, cryogenic temperatures are required for spark production, in order to avoid melting of the electrodes. As superconductivity measurement requires cooling anyway, we had two reasons to set up a system, in which the particles are produced under a temperature slightly above the boiling point of liquid nitrogen.

The particular gallium cluster described by Kresin, et al., containing 56 atoms, has not yet been thoroughly studied (theoretically or experimentally) so it was necessary to make certain assumptions in attempting to characterize these clusters. Firstly, the mobility of the cluster was estimated using the modified Stokes-Millikan law recently evaluated for particles in air with a diameter of 1 to 6.5 nm [4]. This method is based on the mass diameter of the particle, which is defined by the bulk density of the material using the following equations, where  $m$  is the total mass of the particle ( $56 \times 69.723$  amu),  $\rho$  is the bulk density of Ga,  $\lambda$  is the mean free path of the sheath gas (air),  $\mu$  is the viscosity of the sheath gas, and  $d_g$  is the effective gas molecule diameter (0.300 nm for air):

$$d_m = \sqrt[3]{6m/\pi\rho} \quad Kn = \frac{2\lambda}{d_m + d_g}$$
$$Z_{eff} = \frac{3\pi\mu}{e} \cdot \frac{(d_m + d_g)}{1 + Kn \cdot (1.257 + 0.4 \cdot \exp^{(-1.1/Kn)})}$$

The mass diameter of the 56-atom Ga cluster is  $d_m=1.28$  nm. Ku et al. demonstrated that these mobility calculations are most accurate for particles with a mass diameter of 1.5 nm or greater, and their data showed that this equation will under-predict the mobility for smaller particles—that is, the measurable mobility for a particular mass diameter smaller than 1.5 nm will be higher than calculated. Furthermore, the materials used in this paper were ionic liquids, salts, and polymers, and collision diameters we deduce for atomic clusters using their method is not related to the number of atoms in the cluster in any simple way. Equating the mass diameter and the collision diameter, implicitly done in the formulas above, may lead to correct results in one case but not in the other. The estimated mobility of the 56-atom Ga cluster derived this way is  $1.21 \text{ V}/(\text{s}\cdot\text{cm}^2)$ .

Figure 1 depicts the experimental setup used to measure the particle size distribution of atomic clusters produced in the spark discharge system. The high-purity carrier gas is further purified through the use of a molecular sieve (to remove water) and a BTS copper catalyst (to remove oxygen) and then controlled at 30 slm by a helium mass flow controller. The gas is then cooled through a <1 m length of small diameter copper tubing suspended in a dewar filled with liquid nitrogen. Efficient heat exchange was attained due to the fact that the flow was turbulent in this tube, thereby eliminating the resistance to heat transfer within the flow cross-section. Temperature



was controlled by limiting the length of copper tubing in contact with the liquid nitrogen.

The cryogenically cooled gas passes through a tee in which an RTD is used to measure the temperature of the gas immediately prior to entering the spark generator. A capacitor is connected parallel to the spark gap, and a power supply continuously charges this capacitor with the constant current of 1 mA. The discharge voltage is periodically reached, causing 2  $\mu$ s discharges that evaporate electrode material, which condenses into atomic clusters. The capacitance is variable and determines the spark energy and repetition frequency of the discharge, the average power input being constant. The aerosol leaves the spark discharge chamber and enters the photoemission chamber.

In the aerosol photoemission experiment, the clusters in helium suspension are exposed to a UV spectrum that ranges only slightly above the photothreshold of the Ga particles. This way the electron emission probability is very sensitive to the density of states at the Fermi level. The latter changes at the superconducting transition temperature. The change in the average particle charge state is detected (see reference [8]).

The photoemission chamber is a 32 cm long QF40 full nipple (Kurt J. Lesker) with two 6 mm tubes welded to the circumference of the chamber on either end, to provide inlet and outlet for the aerosol. The lamp-side of the nipple is affixed with a UV-transparent fused-silica window, while the other side has a simple glass window. The lamp is an Oriel 68826 Xe flash lamp. This light source was selected because it provided the greatest amount of UV light of all sources which would have fit into the budget. A tunable laser would have been the ideal choice. The bulb was mounted in standard lamp housing with a UV-transparent fused silica focusing lens. A 3 cm diameter UV filter cutting off the spectrum below 230 nm (above 5.4 eV) was inserted in a plexiglass fitting sealed against the UV-transparent window. This is slightly above the photothreshold of the Ga clusters, expected at 5.05 – 5.25 eV. (The precise value is unknown, since the photoelectric enhancement effect depends on the cross-section, or diameter, of the cluster which is estimated as described previously). The lamp housing is purged with a constant flow of nitrogen gas to limit the absorption of UV light by any oxygen present in the path between the bulb and the chamber window—despite the simplified way it is depicted in Figure 1, the entire photoemission chamber is not purged but rather only the lamp-side.

After photoemission the temperature of the gas stream is measured by a separate platinum RTD, and the flow is sent to the differential mobility analyzer (DMA) system described in the project proposal and previous report. An aerosol electrometer (AEM) measures the current of charged particles, calibrated in terms of particle concentration, downstream of the mobility selection device (DMA). Any change in the average charge state induced by photoemission when the temperature crosses the

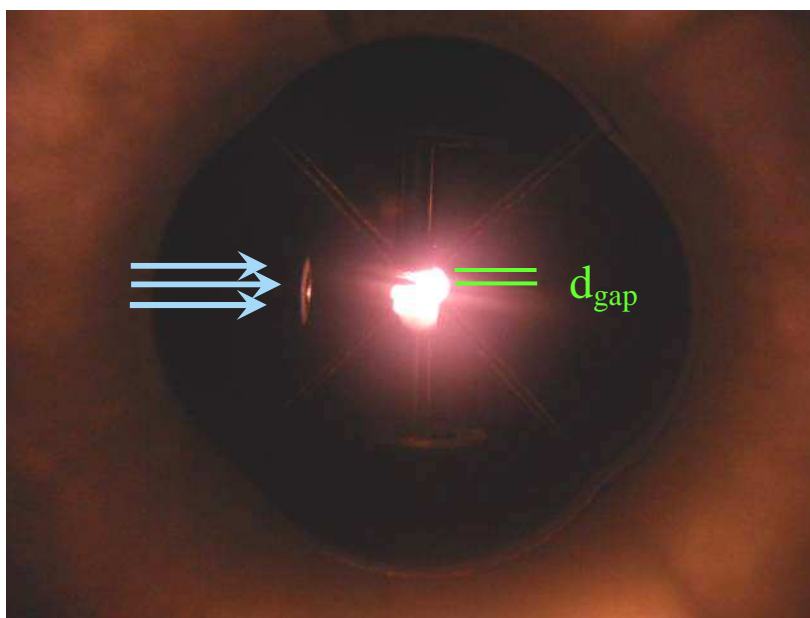
superconducting transition temperature would cause a jump in the AEM current. The search for such a jump during a temperature scan was carried out for a variety of cluster sizes selected by the DMA.

Figure 2 is a picture of the spark discharge in operation. The cooled gas enters the chamber as a jet through a 4mm ID tube positioned near and aimed at the spark discharge. In the right side of the chamber is KF fitting returning to Swagelok for coupling to the photoemission chamber.

One of the several obstacles to obtaining the initial measurements of the size distribution was noise entering the AEM. It was immediately determined that the electromagnetic interference caused by a spark discharge in nitrogen gas, even at a minimum gap separation distance, would cause disturbing oscillations on the AEM signal. This was true even for a nitrogen spark setup elsewhere in the same laboratory space. Helium gas, with its lower breakdown voltage, caused less of a disturbance and was chosen for cryogenic operation of the spark discharge. The AEM also required a separate ground (apart from the spark generator), and a battery power supply to ensure a steady and clean signal. Finally, the spark discharge voltage was maintained below or around 400 V, since noise would become evident in the AEM signal when the electrode gap was increased.

Despite all of these precautions, we were unable to eliminate the noise caused by the UV flash lamp used to stimulate photoemission in the predicted superconducting clusters. This lamp bulb may be filled with air, nitrogen, or another gas with a sufficient breakdown voltage to cause enough noise in our electrometer to prevent accurate measurements. While the signal of the AEM was not driven to its saturation value, the noise was at least twice as high as the signal in the targeted size range (ca.  $10^4 \text{ cm}^{-3}$ , see below). The standard noise level was ca  $1.2 \cdot 10^3 \text{ cm}^{-3}$ .

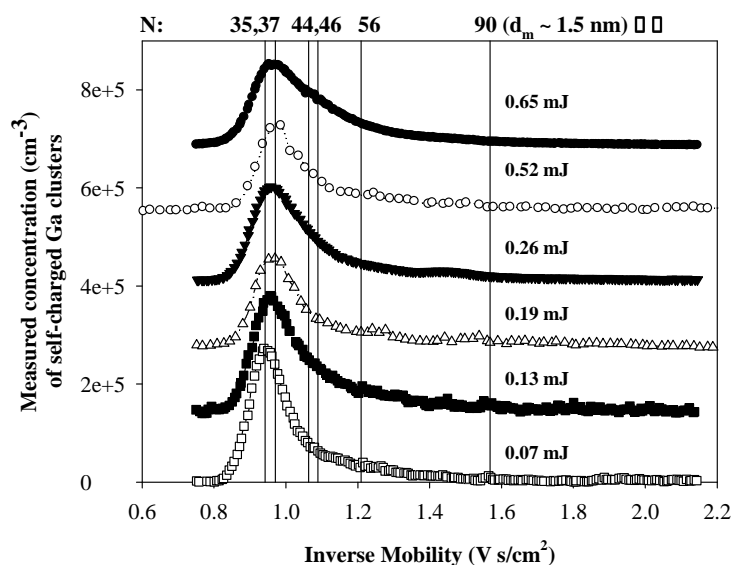
The breakdown voltage of the discharge was maintained at a constant level of 380 V throughout all of the experiments for which data is provided in this report. This was done by modifying the electrode separation distance manually while the DMA program was collecting data, usually lasting



**Figure 2.** Picture of the spark discharge with Ga electrodes.

between two and ten minutes. Since the discharge current was held constant at a minimal value of  $1.00 \pm 0.05$  mA, this has the effect of maintaining a discharge frequency which is inversely proportional to the capacitance of the spark discharge.

Figure 3 shows the results of varying the spark energy on the Ga discharge (at a constant temperature of  $-120$  °C), along with guidelines for atomic cluster sizes based on the calculations of Ku and de la Mora<sup>1</sup>. As mentioned previously, these are only presented to give a rough idea of where these clusters might fall on the inverse mobility



**Figure 3.** Measured size distributions of positive self-charged Ga atomic clusters from the spark discharge.

axis (x-axis). It is immediately apparent that varying the spark energy under this cryogenic temperature has very little effect on the size distribution of Ga clusters, as no new peaks appear. The shape of the distribution becomes somewhat sharper at smaller spark energies, consistent with the hypothesis that providing less energy to the spark discharge should reduce the amount of material liberated into the vapor phase.

We conclude that the peak seen corresponds to a cluster size much more stable than the neighboring sizes. The relative peak broadness is similar to the relative peak broadness obtained for the equal-sized molecules used for mobility calibration ( see [9] for details). The peak seen for Ga and the tail on the large particle side (i.e. large  $Z^{-1}$  side) represents the magic cluster size plus other cluster sizes, but the magic cluster size is strongly dominant. The slight broadening seen for higher spark energies indicates an increase of the contribution of the neighboring sizes. We speculate that the fact that the less stable clusters are largely eliminated is due to an etching effect caused by oxygen impurities remaining in our system, as this has been described by Khanna and Jena [5] for aluminum clusters. For Al, a triple-valent metal just like Ga, a mass spectrometry

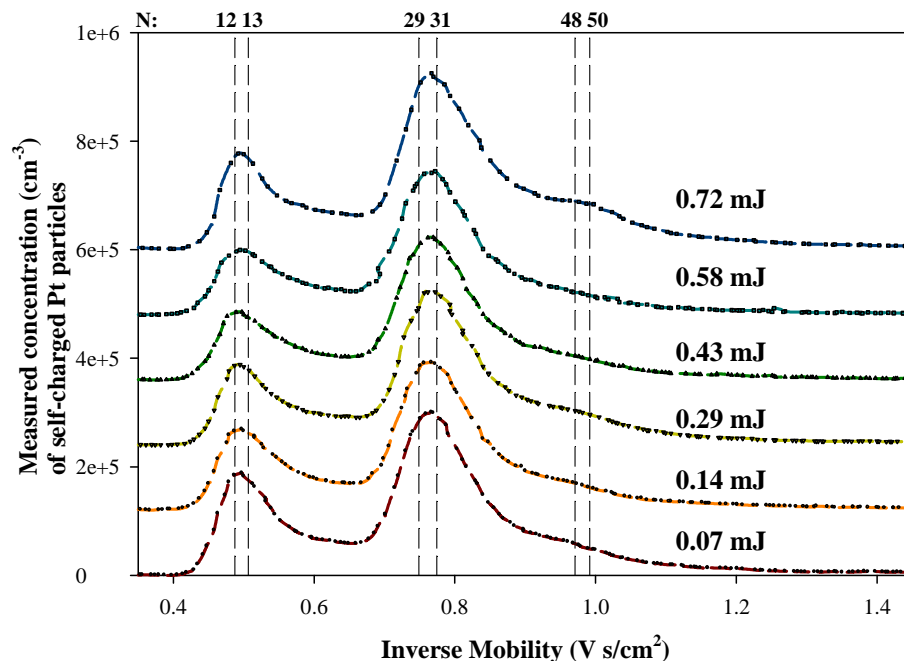
measurement reveals that etching reduces the spectrum to the electronically stable species  $\text{Al}_{13}^-$  and  $\text{Al}_{23}^-$ . In our case, cluster formation and charging by the spark plasma are a complex process. The clusters are certainly present in several charged states as well as the neutral one in the process of their formation. We chose the positive polarity for Ga, and we can presently not assign a magic number to the peak, but our present research is aimed at doing that.

Fig. 3 thus demonstrates that our spark is a quasi-monodisperse source of Ga clusters of a magic size to be determined. Using a DMA for larger sizes we confirmed that no other particle sizes are present up to 100 nm. Knowing the approximate size range that we are probing, we can say with certainty that there is a small but non-zero concentration of particles in the range targeted by Kresin, et al (56 atoms) [1-2]. It would therefore be possible to size-select the effluent of the spark discharge in order to obtain a monodisperse aerosol of these clusters.

Since the photoemission experiments were unsuccessful in our setup, and there was insufficient time and resources to attempt to measure the particles *ex situ* (requires cryogenic isolation in an air-tight container), further experiments were performed using platinum electrodes in the spark generator. With these measurements we will establish our method as a high production rate method for atomic clusters. In addition, these measurements will aid the understanding of the Ga production experiment. Figure 4 depicts the effect of varying spark energy on a *room temperature* discharge using platinum electrodes. The primary peak is near the region estimated at 12 atoms, while the second peak is near 30 atoms. In addition, there is a broad peak in the 48-52 atom range. The spark energy has an effect on the size distribution. This is more clearly shown in this case because of the presence of two clearly defined peaks.

Energy (mJ)	"12" peak (V)	"30" peak (V)	Ratio
0.07	1.509	2.397	1.589
0.14	1.167	2.178	1.867
0.29	1.183	2.259	1.909
0.43	1.004	2.106	2.098
0.58	0.956	2.118	2.217
0.72	1.194	2.530	2.119

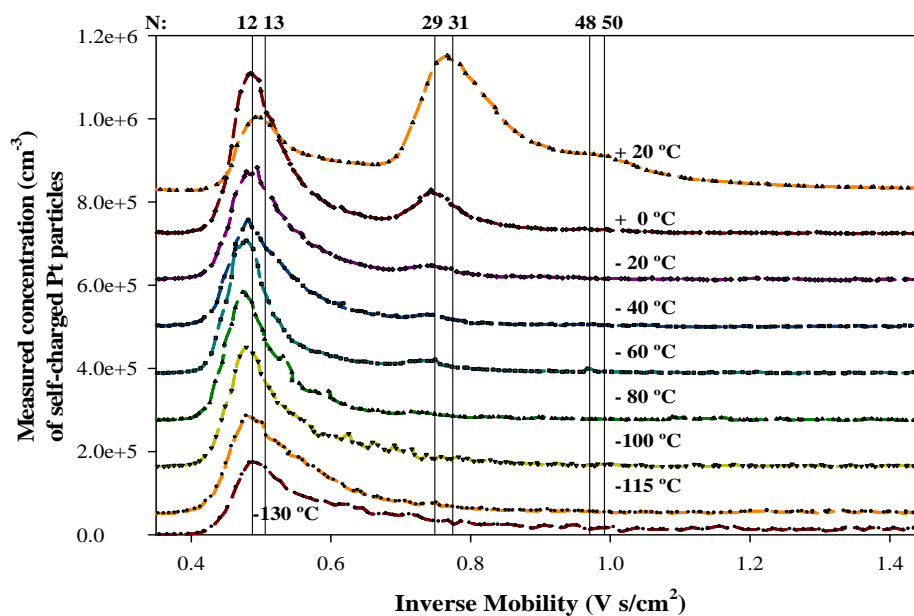
**Table 1.** Peak ratio calculations for Pt clusters as a function of spark energy.



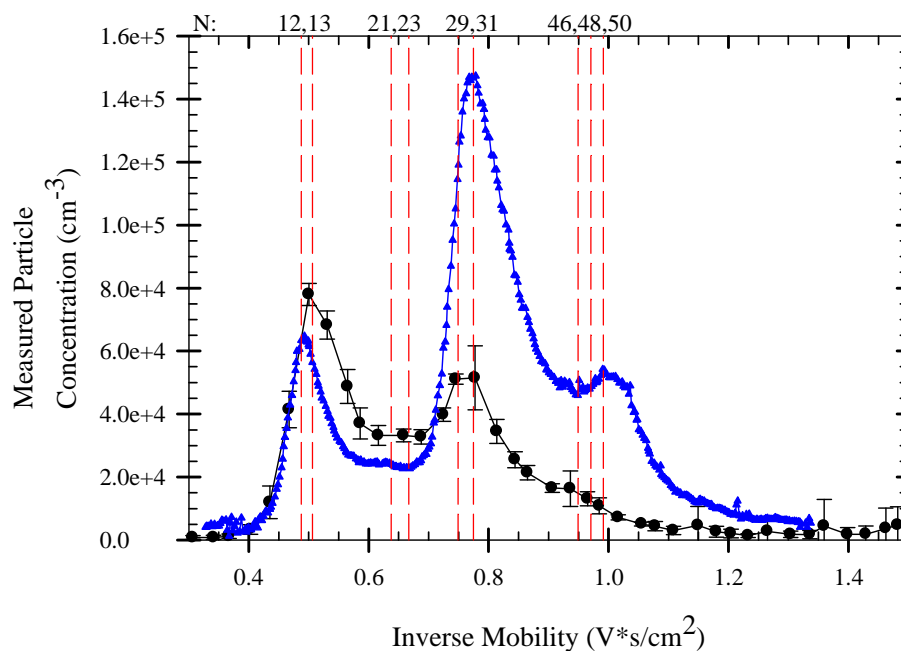
**Figure 4.** Size distribution of positive self-charged atomic clusters at several spark energies, using Pt electrodes at room

Table 1 shows that the ratio of the secondary to the primary peak increases with increasing spark energy. This confirms the hypothesis that increasing the spark energy drives the discharge to produce larger particles. In addition to repeating the experiments on spark energy using Pt electrodes, the effect of gas temperature on the size distribution from these electrodes was evaluated. Figure 5 reveals the much more significant effect that this process variable has on the size distribution of Pt atomic clusters, especially between  $-20$  and  $+20$  °C. At  $20$  °C, as seen in Figure 4 at all spark energies, the primary peak is lower in concentration than the second peak. This ratio is reversed when the gas temperature is  $0$  °C, and below  $-60$  °C, we essentially produce one cluster size. The third peak is eliminated at temperatures below  $0$  °C. Experiments at higher temperatures were not done as they would require line heating to prevent losses due to thermophoresis, but it is predicted that they will lead to the appearance and enhancement of the larger cluster distributions.

All of the above experiments were performed without external charging methods and using a negative polarity high voltage power supply on the central electrode of the DMA, thereby selecting particles which emerge from the spark discharge with a positive charge. Figure 6 shows the distribution of the negative polarity in addition, measured at room temperature and with a spark energy of  $1.4$  mJ. The resolution of the negative distribution on the mobility axis is limited by the positive polarity power supply. The negative distribution looks very similar to the positive one, although the charge state should clearly have an influence on stability. Charge independent magic numbers have also been observed in conventional cluster experiments, in which laser ablation was used for particle production (see e.g.[10]).



**Figure 5** The effect of temperature on the cluster size distribution for Pt



**Figure 6.** Effect of self-charged polarity on Pt cluster size distribution.

These data indicate that the charge state is defined after the cluster formation process is completed. This can happen either by the inclusion of K<sup>+</sup> as suggested in previous work [3], by ionization reactions in the plasma, or from interaction with ions or photons (emitted by excited state species) after the discharge has taken place.

Finally, the cluster mass production rate was estimated. The concentration measured behind the DMA in the peak of the Ga spectrum typically yielded a concentration of  $2.74 \cdot 10^5 \text{ cm}^{-3}$ . Taking into account 90% diffusion losses that would be avoidable by using shorter ducts and an estimated charging probability of 0.01%, this corresponds to a total production rate of around 1 mg/day of Ga clusters. For the Pt particles a similar value is estimated. The charging probability is extrapolated from values obtained for 5 nm particles [7], assuming that the charging probability is surface proportional. As former research proven, much higher charging probabilities (near 100%) are possible by applying aerosol photoemission. Recent research has shown that the spark repetition frequency applied (<100 Hz, depending on the energy per spark) can be increased by a factor of 100. This will boost the cluster production rate to 100 mg/day. A European project, starting on 1 Feb., 2012, has the goal of increasing the present nanoparticle production rate of the spark generator by many orders of magnitude. The methods to be developed will be transferrable to the production of small clusters. Together with the present data we are therefore confident that a production rate of 1 g/day is within reach.

In summary, we were unable to evaluate the superconducting transition temperature in any of the spark-generated atomic clusters but have demonstrated the production of a wide range of atomic cluster sizes with mass production rates around 1 mg/day. The effect of gas temperature and spark energy on the size distribution of Pt-clusters was demonstrated. As reduction of the flow rate leads to particle sizes up to 10 nm, as shown in previous work, we have demonstrated that a spark generator together with a mobility analyzer is a very versatile source for atomic cluster production from the size range of a few atoms to diameters of several nanometers. Under certain conditions, magic number clusters of uniform size are formed by the generator, which makes size selection unnecessary. We assume that chemical etching by traces of oxygen led to the elimination of clusters less stable than the magic number sizes. Thus gas purity is a critical issue, if non-magic number clusters are to be produced. Within a research project to begin on 1 Feb., 2012, we are confident to be able to increase the mass production rate of small atomic clusters up to the g/day range.

## References

- [1] V. Z. Kresin, Y. N. Ovchinnikov, Phys. Rev. B **74**, 024514 (2006).
- [2] V. Z. Kresin, Yu N. Ovchinnikov, Phys. Uspekhi **51**(5), 427-435 (2008).
- [3] C. Peineke, Production and Deposition of Well Defined Aerosol Nanoparticles, Doctoral Thesis, TU Delft (2008).
- [4] B. K. Ku, J. F. de la Mora, Aerosol Sci. & Technol. **43**, 241-249 (2009).

- [5] S.N. Khanna, P. Jena, Phys. Rev. B **51**, 13705 (1995).
- [6] M.F. Jarrold, J.E. Bower, J. Phys Chem. **97**, 1746 (1993)
- [7] N. S. Tabrizi, M. Ullmann, V. A. Vons, U. Lafont, A. Schmidt-Ott, Generation of nanoparticles by spark discharge, J. Nanoparticle Research **11**, 315-332 (2009)
- [8] G. Margaritondo, ed. by Bok et al., The Gap Symmetry and Fluctuations in High- $T_c$  Superconductors, 195 (1998).
- [9] S. Ude, J. Fernández de la Mora, Molecular monodisperse mobility and mass standards from electrosprays of tetra-alkyl ammonium halides, J. Aerosol Science 36 (2005) 1224–1237.
- [10] M. F. Jarrold, J.E. Bower, Mobilities of Metal Cluster Ions  $Al_n^+$  and  $Al_n^{2+}$ : Effect of Charge on Cluster Geometry, J. Phys. Chem..97, 1746-1748, (1993).